of M(III). The ionic radii are sixfold-coordination "oxide" radii (Table I), taken from the compilation of Shannon and Prewitt[14] with the exception of the actinide ions, which are those tabulated by Peterson and Cunningham.[15]

Acknowledgments.—We wish to thank Professor B. B. Cunningham for many helpful discussions.

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The Preparation and Infrared Spectra of *cis*-Dihalodiamminepalladium(II) Complexes

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We report here a new method for the preparation of the three complexes *cis*-$Pd(NH_3)_2X_2$ (X = Cl, Br, I). The preparation of the iodo complex has not previously been fully described.[1] According to Layton, *et al.*,[2] the method of preparation given by Grinberg and Shulman[3] for the *cis*-dichloro and *cis*-dibromo complexes yields impure products that isomerize in the solid state (the bromide more rapidly than the chloride) to the corresponding *trans* complexes. This has also been the experience in our laboratory.[4,5]

Durig and Mitchell[6] developed a method for obtaining more stable specimens of the *cis*-dichloro and *cis*-dibromo complexes that involved carrying out at low temperature the reaction used by Grinberg and Shulman. However, attempts to prepare *cis*-$Pd(NH_3)_2I_2$ by these methods always yielded the *trans* isomer. The main evidence for the identity of the products in the above experiments comes from infrared spectra, as we have not been able to find any solvent that would allow dipole moment measurements to be made. The results given by Perry, *et al.*,[7] which are representative of several reports in the literature, show that, for the chlorides and bromides, there are marked differences between the infrared spectra of the *cis* and *trans* isomers. Other tests that have been used for distinguishing the *cis* from the *trans* isomers are not so conclusive. The *cis*- and *trans*-chloro complexes have both been investigated using X-ray techniques[2,8] but their structures have not been fully established in this way. The uv spectra of *cis*- and *trans*-$Pd(NH_3)_2Cl_2$ in aqueous solution (containing about 10% ethanol) show only small differences.[9] The *cis*-dichloro- and *cis*-dibromodiammines also differ from the respective *trans* isomers in their reactions with potassium iodide solution.[3]

Experimental Section

Tetraamminepalladium(II) perchlorate (I) was prepared as described previously.[1]

***cis*-Dihalodiamminepalladium(II) Complexes.**—A 2.3-g sample of I was dissolved in 75 ml of 0.2 *M* perchloric acid and allowed to stand overnight at room temperature. To the yellow solution was added a concentrated solution of sodium halide whereupon a solid precipitated immediately and was filtered rapidly, washed with water, alcohol, and ether, and dried *in vacuo* over silica gel. The chloro and bromo complexes were dull yellow microcrystalline solids and the iodo complex was brown.

Anal. Calcd for $Pd(NH_3)_2Cl_2$: N, 13.25; H, 2.84; Cl, 33.55. Found: N, 12.9; H, 2.9; Cl, 33.0. Calcd for $Pd(NH_3)_2Br_2$: N, 9.33; H, 2.00; Br, 53.23. Found: N, 9.3, H, 2.0; Br, 52.6. Calcd for $Pd(NH_3)_2I_2$: N, 7.10; H, 1.52; I, 64.39. Found: N, 6.5; H, 1.4; I, 64.4.

On adding NaSCN to the yellow solution, a pink precipitate was deposited. *Anal.* Calcd for $[Pd(NH_3)_4][Pd(SCN)_4]$: C, 9.36; H, 2.34; N, 21.84. Found: C, 9.4; H, 2.3; N, 21.7. No precipitate was formed on adding either $NaNO_2$ or NaOCN.

Infrared measurements (in the range 4000–250 cm^{-1}) were made on Nujol mulls with a Perkin-Elmer 457 spectrophotometer. The uncertainty in the infrared measurements was ±3 cm^{-1}.

Results and Discussion

When an aqueous solution of tetraamminepalladium(II) perchlorate is treated with excess perchloric acid, the aquation of the Pd(II) ion proceeds only as far as the replacement of two ammonia molecules.[1] The addition of chloride ion to a dilute solution of the diaquodiammine results in a rapid change in the uv spectrum, presumably owing to a fast anation reaction and the formation of chloro complexes. Solutions containing different concentrations of acid and chloride differ in their uv spectra and the spectra also change with time. However, in the spectra of several such solutions a shoulder at 290 nm was observed and, as this had been reported[9] to be a feature of aqueous *cis*-$Pd(NH_3)_2Cl_2$, it was suspected that the original diaquodiammine solution probably contained at least some *cis* isomer. Rasmussen and Jørgensen,[10] on the basis of much less slender evidence, have concluded that the diaquodiamminepalladium(II) ion exists mainly in the *cis* form. The present results support this conclusion. As anation reactions of Pd(II) complexes are expected to be fast and as all the known palladium(II) dihalodiammines are only slightly soluble in water, the addition of halide ions to a concentrated aqueous solution of the diaquodiammine would be expected to result in precipitation of the dihalodiammine of the same configuration as the aquo ion. The distinctive infrared absorptions (in the region 1200–300

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cm^{-1}) of the halide complexes described in the Experimental Section are (values in cm^{-1}): chloride: 304 s, 319 s, 476 m, 496 m, 1248 s, 1269 s; bromide: 461 m, 482 m, 1246 s, 1261 s; iodide, sample 1: 429 m, 449 m, 1225 s, 1241 s, 1252 s, 1279 s; iodide, sample 2: 430 m, 451 m, 1227 s, 1241 s, 1252 s, 1281 s.

The values for the chloride and bromide agree very closely with those reported earlier for the *cis* complexes and there seems little doubt that the present samples also have the *cis* configuration. The spectrum of the iodide is similar to what might be expected for *cis*-$Pd(NH_3)_2I_2$. It shows a doublet in the ν(Pd–N) region which continues the trend of decreasing frequencies from Cl to I, a trend that is also apparent in the three *trans* complexes.[7] It also shows several strong peaks in the 1200–1300-cm^{-1} region rather than the single strong peak with a shoulder that seems to characterize the *trans* isomers. However, there are four of these strong peaks rather than the two found in the *cis* chloride and bromide. The presence of additional peaks in the spectrum of the *cis* iodide could be due to its crystal structure being different from those of the *cis* chloride and bromide. Additional peaks could also arise from the presence of impurities such as $[Pd(NH_3)_4][PdI_4]$ and *trans*-$Pd(NH_3)_2I_2$ which show absorptions at 1278 and 1252 cm^{-1}, respectively.

The samples of chloride and bromide complexes showed considerable stability compared with those prepared by earlier methods. In both cases the doubling of the infrared peaks was still strongly evident when the measurements were repeated after 14 months, showing that isomerization had not occurred to any great extent. In the case of the iodide, however, samples showed some evidence of change after 1 month and, after 14 months, exhibited the spectrum of the *trans* isomer. These results tend to confirm the view of Durig and Mitchell[6] that the instability of these *cis* complexes results from the presence of impurities that catalyze the isomerization. Such impurities are less likely to contaminate the product when it is formed rapidly, as in the present experiments, than when it is formed slowly, as in the method used by Grinberg and Shulman. The iodide is probably inherently the least stable of the three *cis* halo complexes and is also probably the least pure of the present samples. The attempt to prepare *cis*-$Pd(NH_3)_2(SCN)_2$ by the present technique resulted in the formation of a pink compound. The ionic dimers $[Pd(NH_3)_4][PdX_4]$ are generally pink and this product was almost certainly the known compound $[Pd(NH_3)_4][Pd(SCN)_4]$. It is interesting that difficulties in preparing *cis*-diacidodiamminepalladium(II) complexes are encountered with several ligands (such as I^-, SCN^-, NO_2^-) that occur high in the *trans*-effect series for Pt(II). The formation of predominantly *cis*-$Pd(NH_3)_2(H_2O)_2^{2+}$ in the aquation of $Pd(NH_3)_4^{2+}$ is also consistent with the Pt(II) *trans*-effect order, $NH_3 > H_2O$.

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High Molecular Weight Boron Sulfides. VI. The Unit Cell of Monoclinic Diboron Trisulfide[1]

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The purpose of this paper is to describe the unit cell of B_2S_3 as obtained from single-crystal Weissenberg and Debye–Scherrer powder X-ray diffraction patterns. Although B_2S_3 has been known for more than a century, crystalline samples were first reported in 1962 by Hagenmuller and Chopin,[2] who prepared them by decomposition of $(HBS_2)_3$ at 100°. These authors apparently could not, however, index the complicated powder pattern. The present authors have used several techniques to prepare B_2S_3 in order to perform a vaporization study of the boron–sulfur system. One of these techniques, as described below, yielded single crystals which were used for the crystallographic investigation.

A powdered mixture of FeS and boron was heated at 700–730° under a steady flow of dried helium in a graphite tube contained in a Vycor tube. White crystals of an average size of $0.1 \times 0.1 \times 0.2$ mm^3 were collected from the cool zones of the graphite tube for several separate preparations.

The limited amount of material collected from separate preparations prevented the complete characterization of each sample: chemical analysis, density, powder diffraction, single-crystal diffraction work, and vaporization studies were not performed on one sample concomitantly, yet the separate results appeared to be consistent.

The melting point was 563 ± 3°. Density measurements gave 1.71 and 1.72 g/cm^3 for a sample having a powder pattern very similar to the pattern listed below.

Chemical analysis of a sample prepared under vacuum slightly contaminated with graphite gave an S:B atomic ratio of 1.506 ± 0.005 with 99.1% recovery.

Single-crystal work was performed on crystals from a third sample. Approximate unit cell parameters and the symmetry properties for B_2S_3 were obtained from two different single crystals by Weissenberg photographs around the two shorter axes. No mirror in the diffraction effects was observed perpendicular to the shortest real axis. Perpendicular to both other axes approximate mirrors appeared to exist, but because the imperfections in the crystals gave rise to streaking and diffuseness of some diffraction spots, a resolution of this contradictory observation could not be made; *i.e.*, whether only one mirror (monoclinic case) or none at all (triclinic case) exists could not be firmly established.

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[1] Abstracted in part from the Ph.D. thesis of H. Y. Chen, submitted to the University of Kansas, 1969.

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